



Short communication

Composite contacting interlayer as cathode current collector for anode-supported planar solid oxide fuel cell stack



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HIGHLIGHTS

- A composite material was used as cathode current collector to replace noble metals.
- The stack with silver as cathode current collector has higher power density.
- The stack with the composite interlayer displays the good long-term stability.

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ABSTRACT

A composite used as cathode current collecting material to replace noble metal for anode-supported solid oxide fuel cells is fabricated and its properties are characterized. Current collecting for the cathode is achieved by forming a composite contacting interlayer to bind the cathode and interconnect together. The results indicate that, with the existence of the glass, the change of the conductivity may be attributed to the glass used as sintering-aid to raise the relative density of the sample calcined at 1000 °C for 1 h. The composite contacting interlayer can well adhere to the contact surface and the area specific resistances is 0.024 Ω cm² for composite coated interconnect. The cell stack with composite contacting interlayer as cathode current collector shows more stable performance after ten thermal cycling tests from 30 to 800 °C.

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1. Introduction

Solid oxide fuel cells (SOFCs) are an energy conversion device which can directly convert chemical energy into electrical energy with high efficiency and low to zero emission [1,2]. The cells can be fabricated in a variety of designs, such as tubular, planar, etc. [1]. In the planar design, chromia-forming ferritic alloy and Cr-base alloy have been widely used as interconnect materials at an intermediate temperature range of 650–800 °C [3,4]. In order to reduce the contact resistance between the interconnect material and the anode, a nickel mesh was added to the anode side. On the cathode side, a cathode contacting layer, such as silver and platinum, was applied to ensure electrical contact [5].

The performances of a SOFC depend not only on the internal resistance of the positive-electrolyte-negative (PEN), but also on the electrical contacts between PEN and interconnect [6]. It has

been reported that the electrochemical performance of electrodes is sensitive to the physical and chemical nature of the current collectors [7–9]. Therefore, it may be expected that single cells with current collectors will exhibit different electrochemical performances. Presently, electrical current collectors formed by noble metals, such as platinum or silver, are often applied on top of electrodes to minimize contact resistance [6,10]. In many studies, because of easily printing and firing to obtain good adherence to the electrodes, silver close to the practical current collector in SOFC stacks has been selected as the cathode current collectors at operation temperatures less than 800 °C [6,9–14]. In order to further modify the performance of current collector, Bi₂O₃-added silver paste as a cathode current collector was widely studied [15–17]. Due to having a low melting temperature of 823 °C and a much higher oxygen ionic conductivity than 8 mol% Y₂O₃-stabilized ZrO₂ (YSZ) [18], Bi₂O₃ may improve the cathode-electrolyte interface by reducing interfacial resistance [19]. Nevertheless, it was reported that, for metal silver and platinum as current collector, cell performance at the initial operation time was more than that of La_{0.4}Sr_{0.6}CoO₃ and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃, but the performance

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degradation rate is obviously more than that of $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ as a cathode current-collector. The performance degradation of the Ag–Pd and Pt pastes was caused by increased polarization resistance due to metal particle sintering [6]. The influence of the structure of current collector on electrochemical properties was reported [8], in which a nickel mesh on an anode side was used as current collector; the electrochemical properties did not vary with time. This paper presents the results of these studies whereby main emphasis was put on the composite consisted of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and glass used as cathode contacting interlayer material to replace noble metal as cathode current collector. Thereby not only the conductivities and interface resistances of the composite but also the performance of the cell stack was taken into account.

2. Experimental

2.1. Preparation of powders

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) powder was prepared by solid–liquid reaction method. The starting materials used were Mn_2O_3 (99.9% purity), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity), and $\text{Sr}(\text{CO}_3)_2$ (99.9% purity). Stoichiometric amounts of the metal nitrate solution, Mn_2O_3 powder and suitable citric acid were mixed and ball-milled for 12 h, and then calcined at 600 °C for 2 h to form a precursor. After ball-milling for 12 h, the precursor was calcined at 1000 °C for 5 h, converting the precursor materials into fine powder of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

The glass based on the $\text{BaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}-\text{B}_2\text{O}_3$ system was made by a conventional glass-making technique. All the original reagents, BaO , Al_2O_3 , SiO_2 , KNO_3 , HBO_4 , etc., were of chemical grade. They were mixed in a ball mill, melted, and held at 1400–1500 °C for 4 h, then poured onto steel molds, and finally crushed into powders.

2.2. Preparation of samples

LSM was mixed with the glass powder of 10–40 wt.% and form a composite. The slurry was prepared by mixing the composite (LSM:glass = 75:25 wt.%) with ethylene glycol and ball-milling for 8–12 h. The slurry was applied onto a LSM pellet and the interconnect with $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ (LSC) coating layer prepared by air plasma spraying (Praxair3710), and then co-sintered at 900–1000 °C for 1 h. The LSM pellet or bar was shaped by pressing the LSM powder confined in a rigid die and fired at 1000–1400 °C for 5 h. The anode-supported was made via a tape-casting process with a cermet of NiO and YSZ . It was pre-sintered at 1300 °C, and an YSZ electrolyte was a tape-casting process on the surface of the anode-supported and co-fired at 1400 °C. The electrolyte layer and anode-supported were about 15 and 400 μm thick, respectively. A cathode composed of LSM and YSZ was coated on the YSZ electrolyte and calcined at 1150 °C for 2 h. The cathode has a thickness of about 50 μm .

2.3. Characterization of electrochemical performances

The relative densities of the samples were measured using the standard Archimedes method. The conductivity of rectangular bar specimens (35 mm × 5 mm × 5 mm) calcined at 1000–1400 °C for 5 h was studied from 600 to 800 °C using standard DC four-probe technique (Model: 34401, H.P.). The samples were analyzed by scanning electron microscope (S-4800, Japan). The impedance was measured using an electrochemical station (IM6EX, Zahner) in the frequency range of 0.1–10⁶ Hz with AC amplitude of 10 mV. The measurement setup is shown in Fig. 1. Both surfaces of the samples

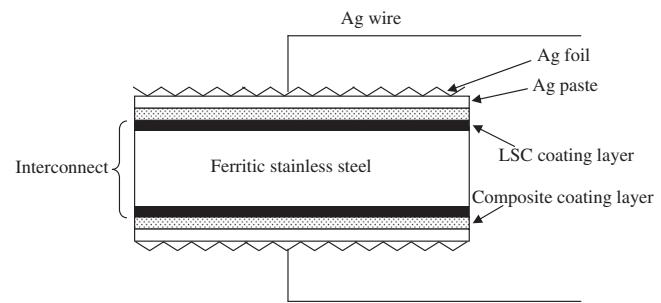


Fig. 1. Schematic setup for area specific resistance measurement.

were covered by Ag paste, and then Ag foils were placed on the top of the pastes as current collectors. The structure of the cell stack is showed in Fig. 2. For the interconnect, the composite slurry was coated on one side to form a composite contacting interlayer of about 60 μm thick and Ag paste was coated on the other side. For single cell of 60 mm × 60 mm, Ag paste was coated on the anode side. The sealant is a glass mainly consisting of BaO , SiO_2 , B_2O_3 , Al_2O_3 , etc. The sealant bars were shaped by pressing the powder confined in a rigid die and pre-fired at 700 °C for 2 h. Interconnects, sealant bars and single cell were in turn stacked and co-sintered under pressure at 950 °C for 1 h and form a stack with one single cell. The measurement of the stack was tested in a self-assembled cell testing system. Thermal cycle process is form 30–800 °C for 10 h. Humidified (3% H_2O) hydrogen, which can be achieved by bubbling H_2 through water at about 25 °C, was used as fuel and air as oxidant.

3. Results and discussion

3.1. Conductivity

The temperature dependence of conductivity of the samples calcined at different temperatures is shown in Fig. 3. From Fig. 3, at 800 °C, the conductivity of the composite of 25 wt.% glass calcined at 1000 °C for 1 h is 86.8 S cm^{-1} , which is more than that of LSM calcined at 1000 °C for 5 h and close to the that of LSM calcined at 1350 °C for 5 h, indicating that, due to the existence of glass, the conductivity obviously increases. As the glass content up to 40 wt.%, calcined at 1000 °C for 1 h, the conductivity is 62.1 S cm^{-1} . This is because the insulated volume fraction of the glass phase increases. The cross-section morphology of the composite of 25 wt.% glass calcined at 1000 °C for 1 h is shown in Fig. 4. Some closed pores are observed and a dense sintered LSM is formed. The relative density is 86% for LSM calcined at 1350 °C, 72% for LSM calcined at 1000 °C

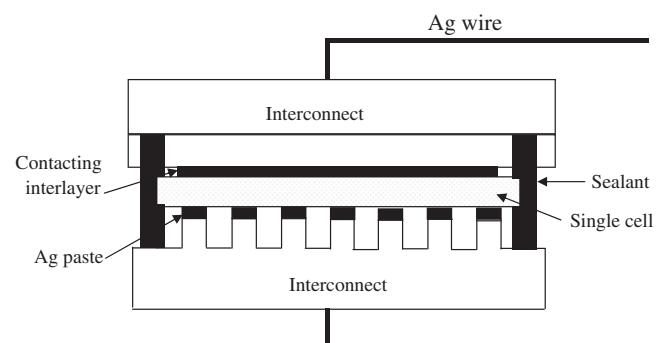


Fig. 2. The structure of the cell stack with composite contacting interlayer as cathode current collector.

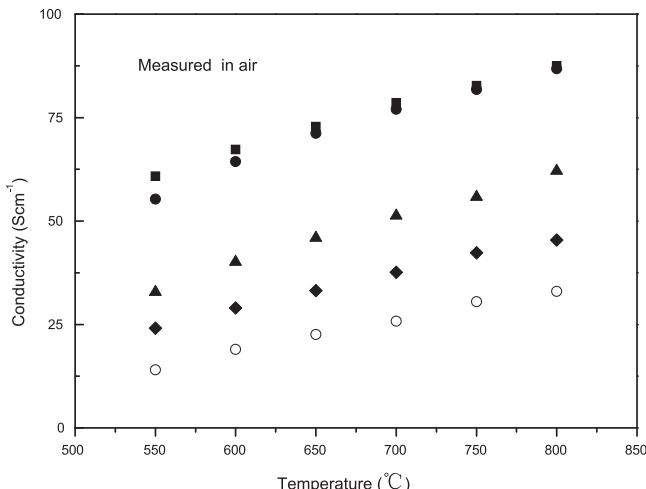


Fig. 3. Temperature dependence of conductivity of the samples calcined at different temperatures. (■: LSM calcined at 1350 °C for 5 h, ●: composite of 25 wt.% glass calcined at 1000 °C for 1 h, ▲: composite of 40 wt.% glass calcined at 1000 °C for 1 h, ◆: composite of 10 wt.% glass calcined at 1000 °C for 1 h, ○: LSM calcined at 1000 °C for 5 h).

and 92% for the composite of 25 wt.% glass calcined at 1000 °C. The relative density of the composite of 25 wt.% glass calcined at 1000 °C is more than that of LSM calcined at 1350 °C. As lack of the glass, the sample did not fully sinter, the conductivity is low. Therefore, the conductivity depends on the relative density and volume fraction of the insulated phase. As the glass content increasing, the glass forms more insulated phase and reduced the conductivity. At the same time, due to the existence of the glass, the liquid phase sintering may play an important role and the relative density increases with the glass content increasing. At 1000 °C for 1 h, the composite of 25 wt.% glass almost gets densified. More glass content will result in the decrease of the conductivity. In conclusion, adjusting glass content in the composites is an effective approach to acquire high conductivity at lower calcination temperature. But, if the glass impregnates the porous electrode, the cell performance declines. To solve this problem, the softening temperature and crystallization temperature of the glass are rigorously controlled. In this study, the softening temperature is more than 750 °C, and the crystallization temperature is about 900 °C. When heating more than 900 °C, the crystal phases fully precipitate. At

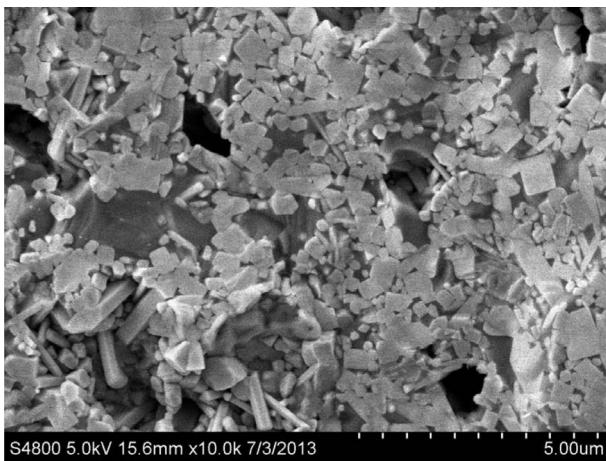


Fig. 4. The cross-section morphology of the composite of 25 wt.% glass calcined at 1000 °C for 1 h.

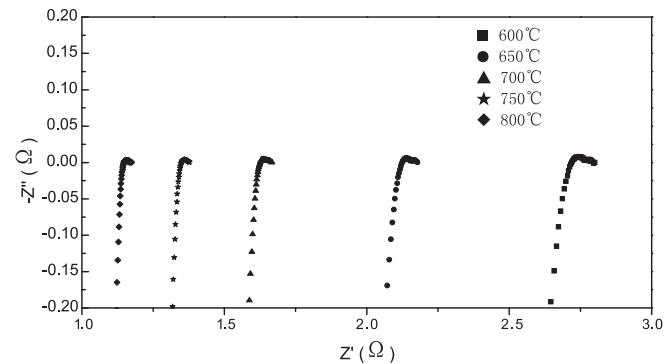


Fig. 5. Impedance spectra for the composite coated interconnect, measured from 600 to 800 °C.

the same time, the precipitated crystals enhance the viscosity of the glass to inhibit the glass impregnating the porous electrode at lower temperature [20]. Besides, the coefficient of thermal expansion (CTE) of the glass should match with that of the LSM. In this study, after heating the glass to 1000 °C for 5 h and crystals fully precipitating, the CTE of the material is controlled at $10-12 \times 10^{-6} [\text{K}^{-1}]$, which is close to $11.7 \times 10^{-6} [\text{K}^{-1}]$ of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ [21], to reduce the stress produced during heating and cooling cycles.

3.2. Electrochemical performance of the composite contacting interlayer

The impedance spectra of the composite coated interconnect, measured from 600 to 800 °C is shown in Fig. 5. The low and high frequency real-axis intercepts correspond to the total resistance (R_{total}) and ohmic resistance (R_{ohm}), respectively. The difference between the low and high frequency intercepts on the real axis can be interpreted as the polarization resistance (R_{pol}) [22]. The Area specific resistances (ASRs) of interconnect and composite coated interconnect are shown in Fig. 6. At 800 °C, the ASR is $0.023 \Omega \text{cm}^2$ for interconnect, $0.024 \Omega \text{cm}^2$ for composite coated interconnect, the difference is $0.001 \Omega \text{cm}^2$. The same experimental procedure is conducted. The composite slurry is coated on the two sides of the LSM pellet and calcined at 950 °C for 1 h. The result shows the R_{pol} of the sample is almost zero. The cross-section morphology of the

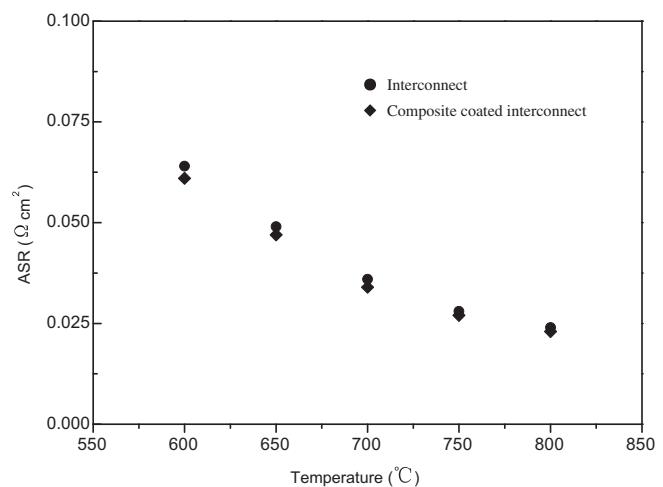


Fig. 6. The area specific resistances (ASRs) of interconnect and composite coated interconnect, measured from 600 to 800 °C.

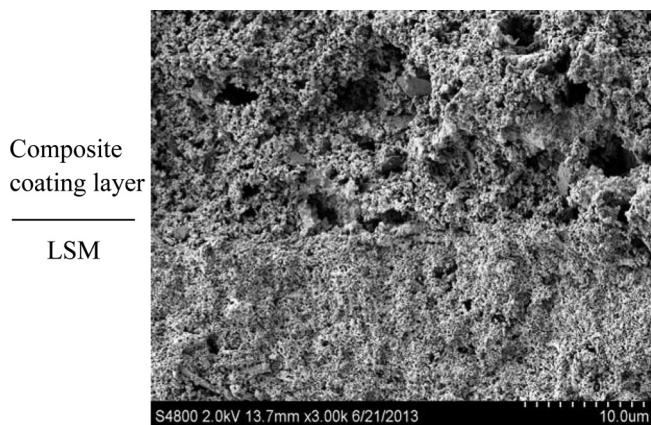


Fig. 7. The cross-section morphology of composite coated LSM, calcined at 950 °C for 1 h.

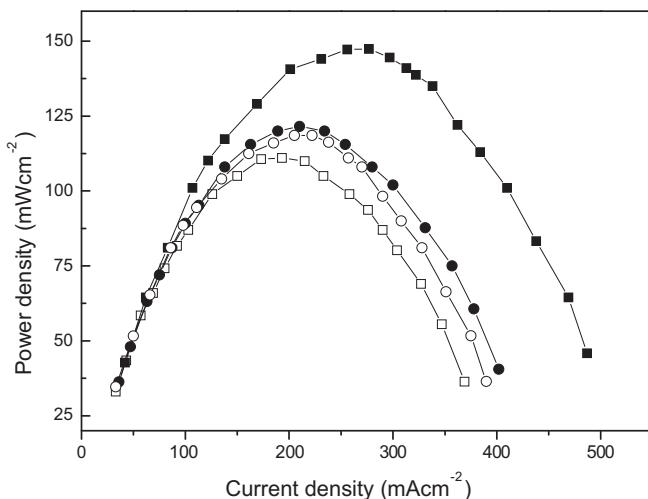


Fig. 8. Power density as a function of current density for cell stacks with different cathode current collectors at operating temperatures of 800 °C. (■: Ag paste as cathode and anode current collectors, □: Ag paste as cathode and anode current collectors after thermal cycles of ten times ●: Ag paste as anode current collector, composite contacting interlayer as cathode current collector, ○: Ag paste as anode current collector, composite contacting interlayer as cathode current collector after thermal cycles of ten times).

sample with composite coating layer on the LSM pellet is shown in Fig. 7. The composite coating layer is well adhered to the LSM substrate. No micro cracks are observed in the interface. In addition, in this study, the influence of the surface microstructure of the LSC coating layer on the ASRs has been confirmed. Therefore, the LSC coating layer prepared by plasma spraying method is modified by dip coating LSM slurry to form a thin LSM layer. After firing at 1000 °C for 2 h, the LSM layer used as a support, on which the composite slurry is coated.

3.3. Performance of cell stacks

The power density as a function of current density for cell stacks with different types of cathode current collectors at operating

temperatures of 800 °C is shown in Fig. 8. The maximum power density is 147.4 mW cm⁻² for Ag paste, 121.5 mW cm⁻² for contacting interlayer. The cell stack with Ag paste gives the best performance. After ten thermal cycling tests from about 30 to 800 °C, the maximum power density for composite interlayer is 118.5 mW cm⁻², showing a more stable performance. The maximum power density for Ag paste is 110 mW cm⁻², indicating significant performance degradation.

4. Conclusion

It is apparent from this study that the design of the cell stack with composite contacting interlayer as cathode current collector is feasible. The results show that the conductivity of the composite calcined at 1000 °C is 86.8 S cm⁻¹, which is close to that of LSM calcined at 1350 °C for 5 h. The ASR values of composite coated interconnect and interconnect is 0.024 and 0.023 Ω cm², respectively. The polarization resistance (R_{pol}) of coated LSM is almost zero. The maximum power densities of the cell stacks with Ag paste and composite contacting interlayer are 147.4 and 121.5 mW cm⁻², respectively. After thermal cycles of ten times, the maximum power densities of the cell stacks with Ag paste and composite interlayer are 110 and 118.5 mW cm⁻², indicating that composite contacting interlayer as cathode current collector displays the good long-term stability.

Acknowledgments

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References

- [1] A.B. Stambouli, E. Traversa, *Renewable Sustainable Energy Rev.* 6 (2002) 433–455.
- [2] B.C.H. Steele, *Nature* 414 (15) (2001) 345–352.
- [3] J.B. Goodenough, *Ann. Rev. Mater. Res.* 33 (2003) 91–128.
- [4] W.Z. Zhu, S.C. Deevi, *Mater. Sci. Eng. A* 348 (2003) 227–243.
- [5] S.P. Jiang, *J. Power Sources* 124 (2003) 390–402.
- [6] J.H. Kim, R.H. Song, D.Y. Chung, S.H. Hyun, D.R. Shin, *J. Power Sources* 188 (2009) 447–452.
- [7] C. Chervin, R.S. Glass, S.M. Kauzlarich, *Solid State Ionics* 176 (2005) 17–23.
- [8] M. Guillodo, P. Vernoux, J. Fouletier, *Solid State Ionics* 127 (2000) 99–107.
- [9] S.P. Simmer, M.D. Anderson, L.R. Pederson, J.W. Stevenson, *J. Electrochem. Soc.* 152 (2005) A1851–A1859.
- [10] T. Tsai, S.A. Barnett, *Solid State Ionics* 93 (1997) 207–217.
- [11] W.A. Meulenbergh, O. Teller, U. Flesch, H.P. Buchkremer, D. Stover, *J. Mater. Sci.* 36 (2001) 3189–3195.
- [12] S.P. Jiang, J.G. Love, L. Apateanu, *Solid State Ionics* 160 (2003) 15–26.
- [13] Z.P. Shao, S.M. Haile, *Nature* 431 (2004) 170–173.
- [14] T. Suzuki, M. Awano, P. Jasinski, V. Petrovsky, H.U. Anderson, *Solid State Ionics* 177 (2006) 2071–2074.
- [15] Y.H. Gong, W.J. Ji, L. Zhang, B. Xie, H.Q. Wang, *J. Power Sources* 196 (2011) 928–934.
- [16] A. Chakraborty, H.S. Maiti, *Ceram. Int.* 25 (1999) 115–123.
- [17] V.V. Kharton, F.M.B. Marques, A. Atkinson, *Solid State Ionics* 174 (2004) 135–149.
- [18] P. Shuk, H.D. Wiemhofer, U. Guth, W. Gopel, M. Greenblatt, *Solid State Ionics* 89 (1996) 179–196.
- [19] T. Tsai, S.A. Barnett, *Solid State Ionics* 98 (1997) 191–196.
- [20] J.W. Fergus, *J. Power Sources* 147 (2005) 46–57.
- [21] M. Mori, *Solid State Ionics* 174 (2004) 1–8.
- [22] T. Horita, K. Yamaji, N. Sakai, H. Yokokawa, A. Weber, E.I. Tiffey, *Electrochim. Acta* 46 (2001) 1837–1845.